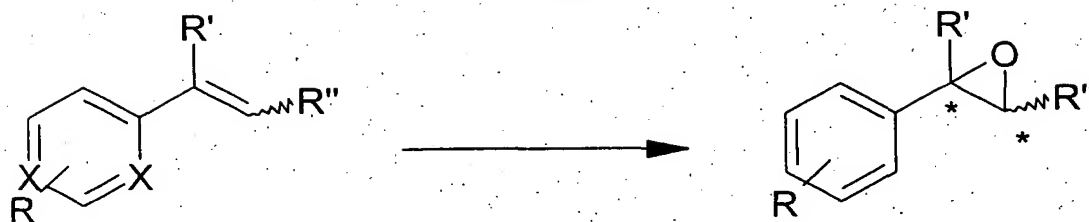


Figure 1: In vitro regeneration of styrene monooxygenase (StyA). $[\text{Cp}^*\text{Rh}(\text{bpy})(\text{H}_2\text{O})]^{2+}$ catalyzed regeneration (upper) compared to a reductase-catalyzed setup (e.g. utilizing the native reductase StyB) with NAD(P)H regeneration.

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R = H, 3-methyl, 4-methyl, 4-F, 4-Cl, 4-Br, 3-Br, 3-NO₂

R' = H, methyl

R'' = H, *trans*-methyl

X = C, N

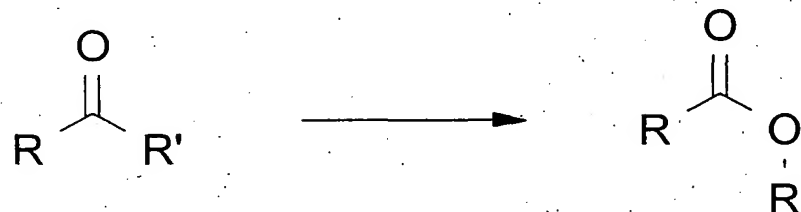
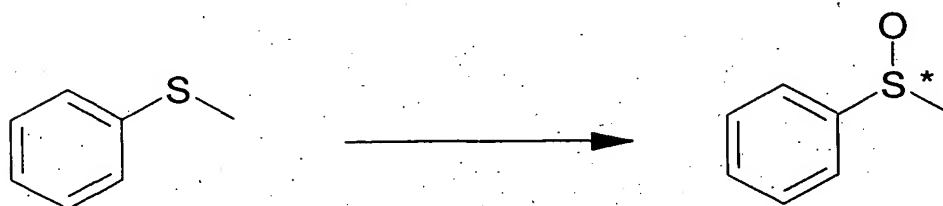
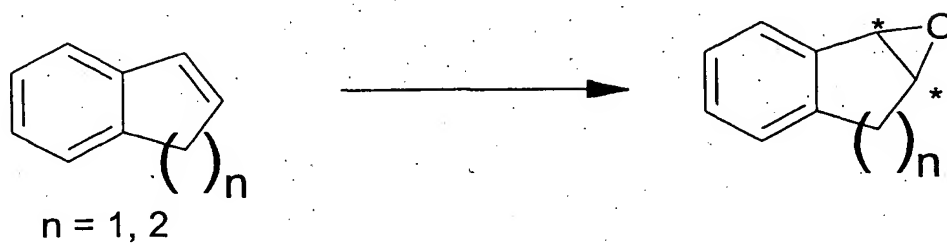


Figure 2: Examples for StyA-catalyzed oxidation reactions.

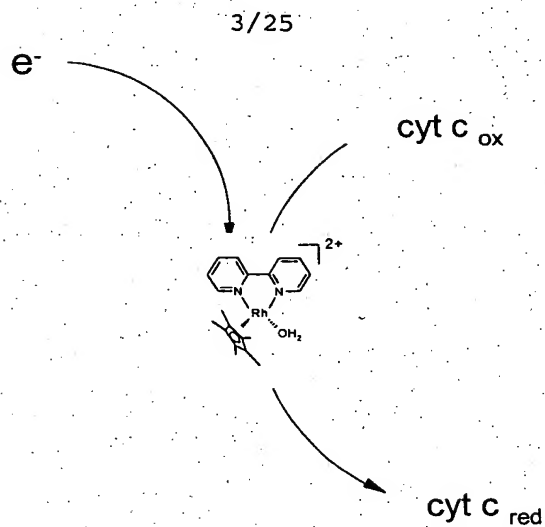


Figure 3: $[Cp^*Rh(bpy)H]^+$ catalyzed and formate driven reduction of CytC. Electrons are derived either from chemical reductants (such as formate) or from the cathode.

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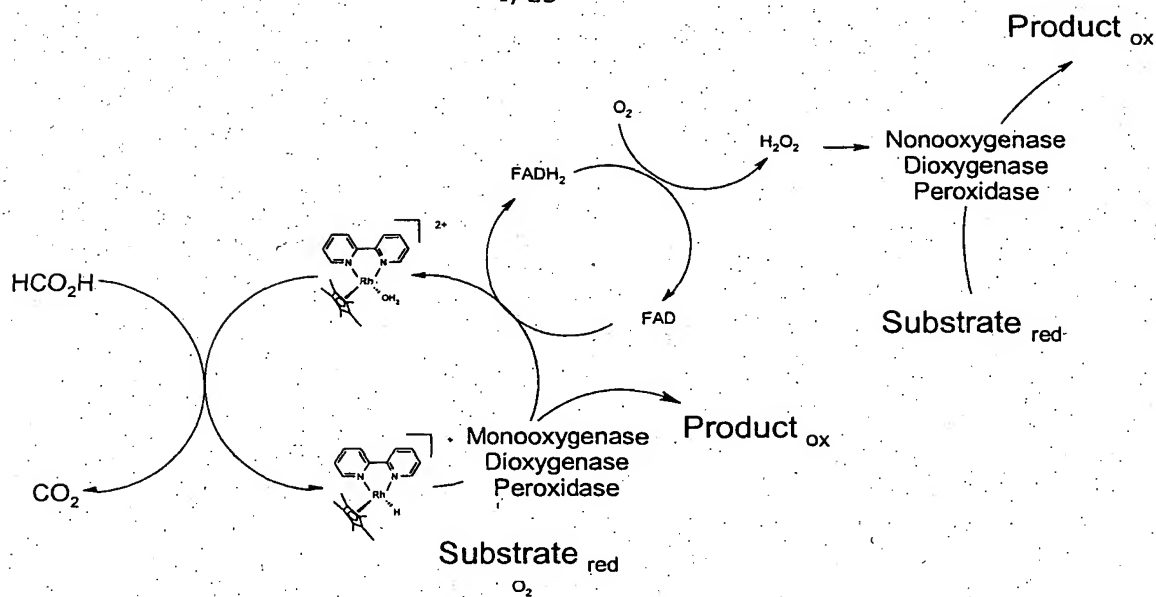


Figure 4: Summarized regeneration pathways of *in vitro* regeneration of monooxygenases and peroxidases.

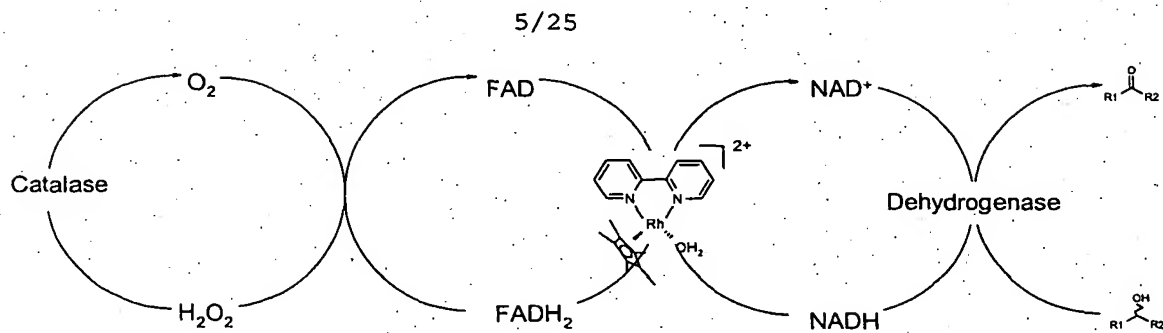


Figure 5: Transhydrogenation from NAD(P)H to FAD (FMN) catalyzed by $\text{Cp}^*\text{Rh}(\text{bpy})(\text{H}_2\text{O})^{2+}$ and its application to dehydrogenase catalyzed oxidation reactions.

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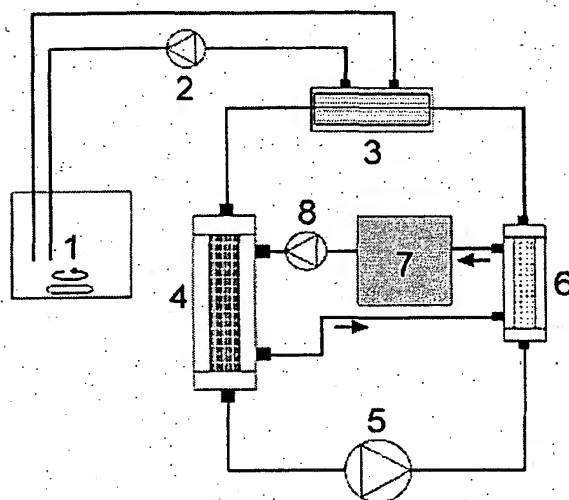


Figure 6: Schematic setup of a compartmented electrochemical setup with immobilized biocatalyst. (1) stirred reservoir for substrates and products in a suitable solvent; (2) pump; (3) hollow-fibre module; (4) flow-through electrolysis cell (connected to a potentiostat); (5) pump; (6) immobilized biocatalyst (7) thermostat (8) pump.

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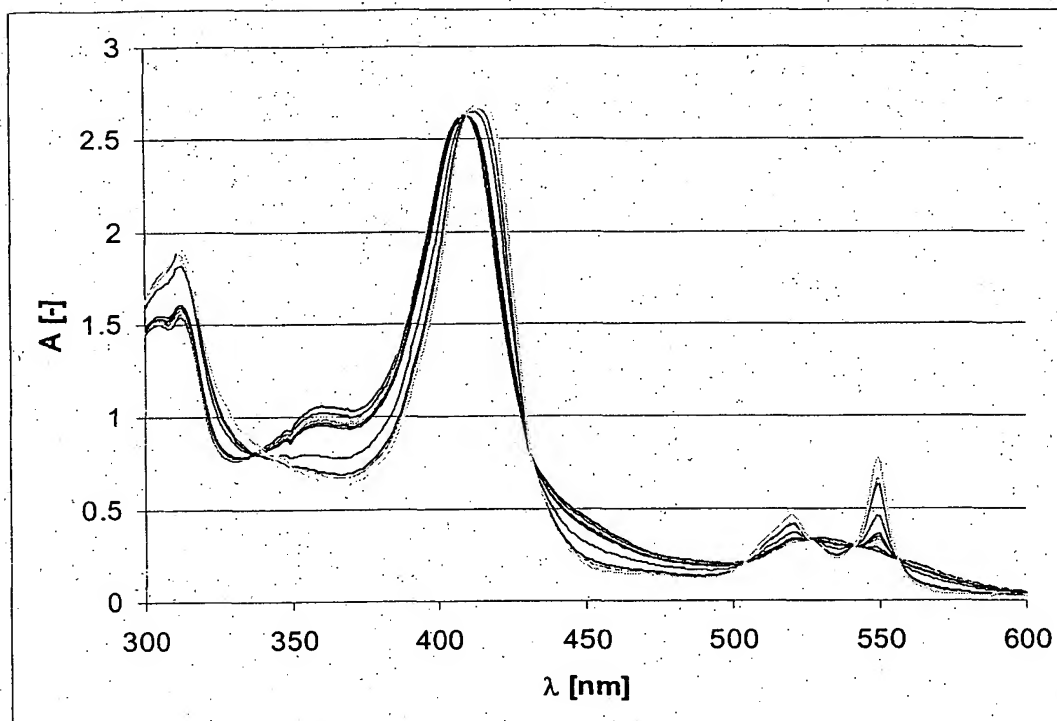


Figure 7: UV-spectra of CytC while incubation with hydrogen peroxide.

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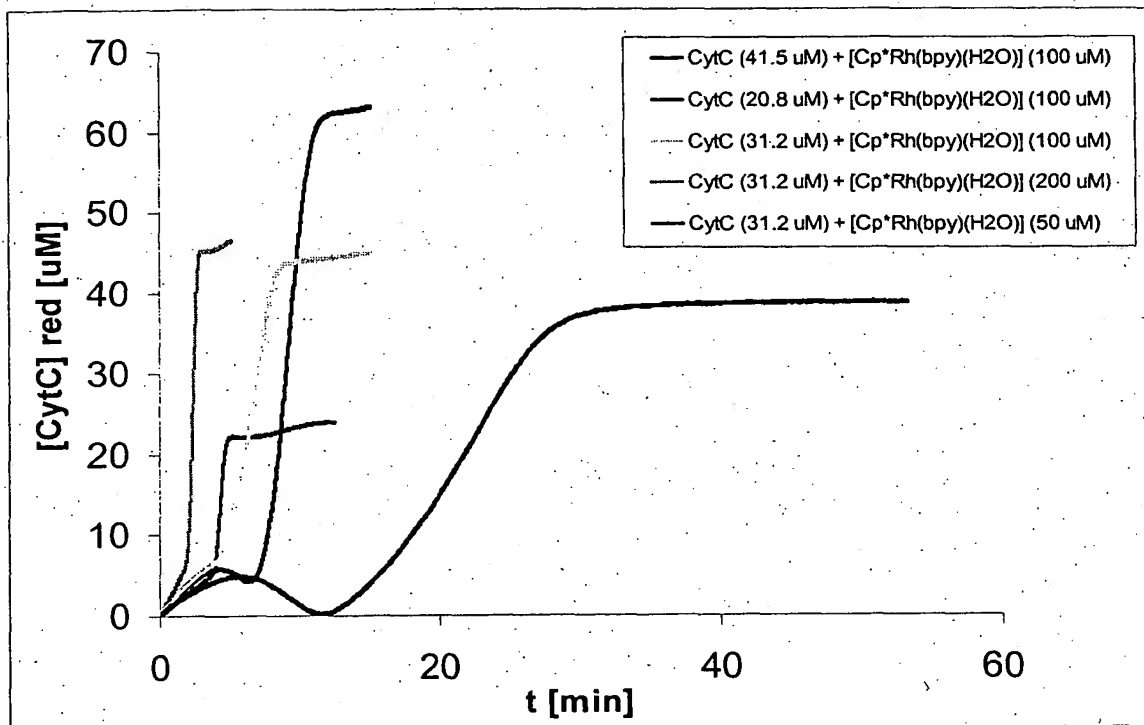


Figure 8: Experiments on varying $c([\text{Cp}^*\text{Rh}(\text{bpy})(\text{H}_2\text{O})]^{2+})$ and $c(\text{CytC})$.

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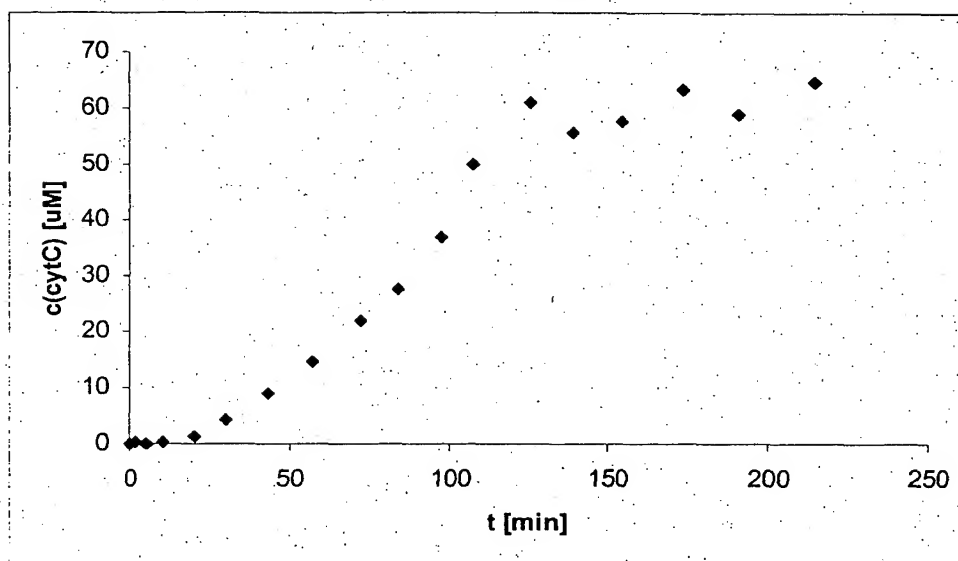


Figure 9: Sub-stoichiometric use of $[\text{Cp}^*\text{Rh}(\text{bpy})(\text{H}_2\text{O})]^{2+}$.
 $c([\text{Cp}^*\text{Rh}(\text{bpy})(\text{H}_2\text{O})]^{2+}) = 10 \mu\text{M}$, $c(\text{cytC}) = 80 \mu\text{M}$, $c(\text{NaHCO}_2) = 150 \text{ mM}$,
 $T = 30 \text{ }^\circ\text{C}$, degassed buffer.

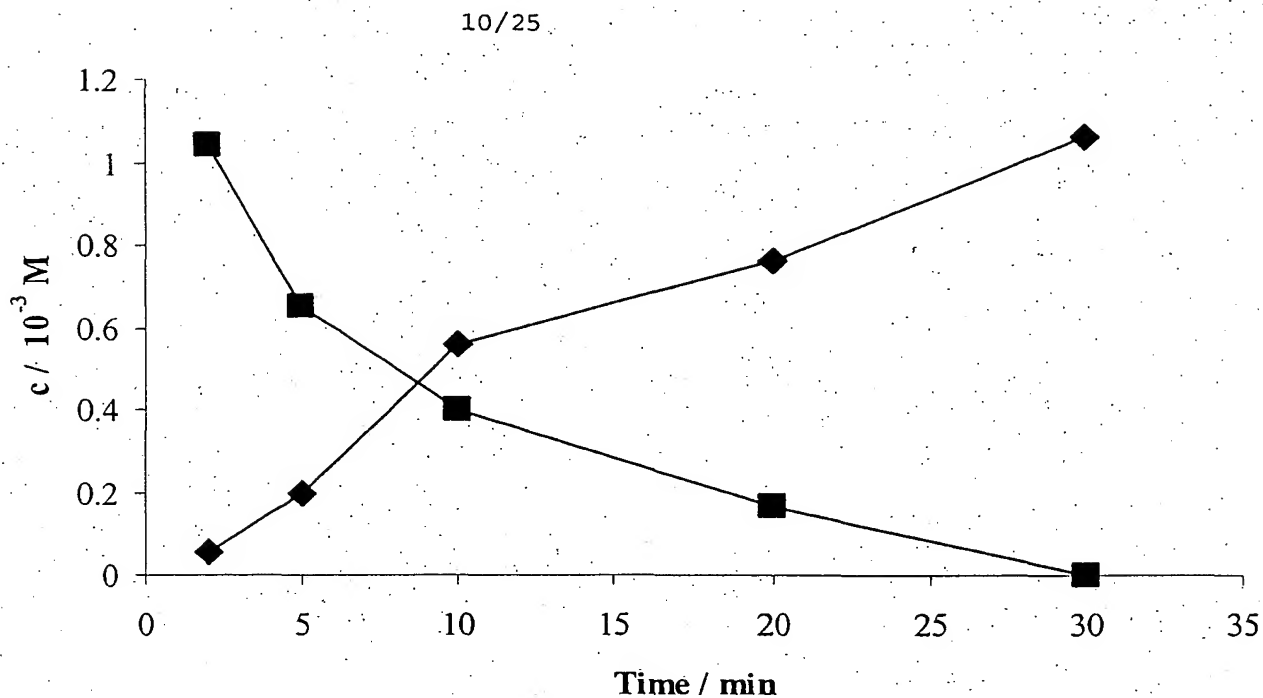


Figure 10: Time course of $[\text{Cp}^*\text{Rh}(\text{bpy})(\text{H}_2\text{O})]^{2+}$ -driven and StyA-catalyzed epoxidation of styrene. Styrene oxide (—◆—); styrene (—■—).
 $T = 37^\circ\text{C}$; $c(\text{NaHCO}_2) = 0.15 \text{ M}$; $c([\text{Cp}^*\text{Rh}(\text{bpy})(\text{H}_2\text{O})]^{2+}) = 2 \times 10^{-4} \text{ M}$;
 $c(\text{FAD}) = 5 \times 10^{-5} \text{ M}$; $c(\text{FMN}) = 5 \times 10^{-6} \text{ M}$; catalase = $28 \text{ U} \times \text{ml}^{-1}$; c_0
 (styrene) = $2 \times 10^{-3} \text{ M}$; $c(\text{StyA}) = 50 \mu\text{g} \times \text{ml}^{-1} = 1.16 \times 10^{-6} \text{ M}$.

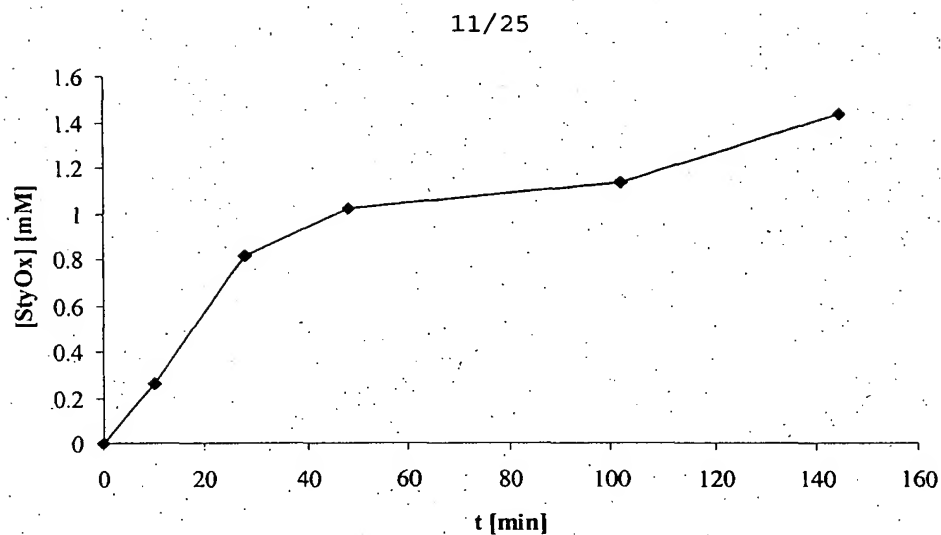


Figure 11: Styrene oxide formation in the presence of neat styrene as 2nd organic phase (substrate & product reservoir).

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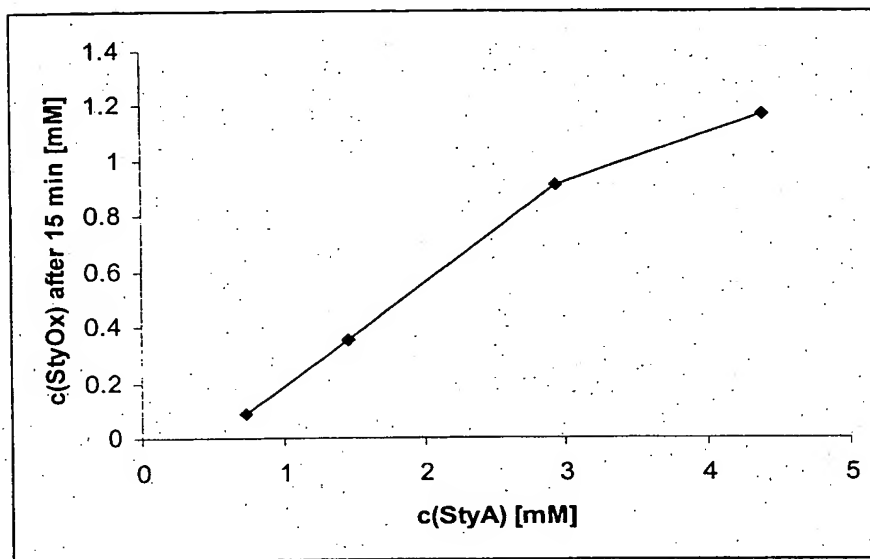


Figure 12: Styrene oxide concentration after 15 min incubation on variation of c(StyA).

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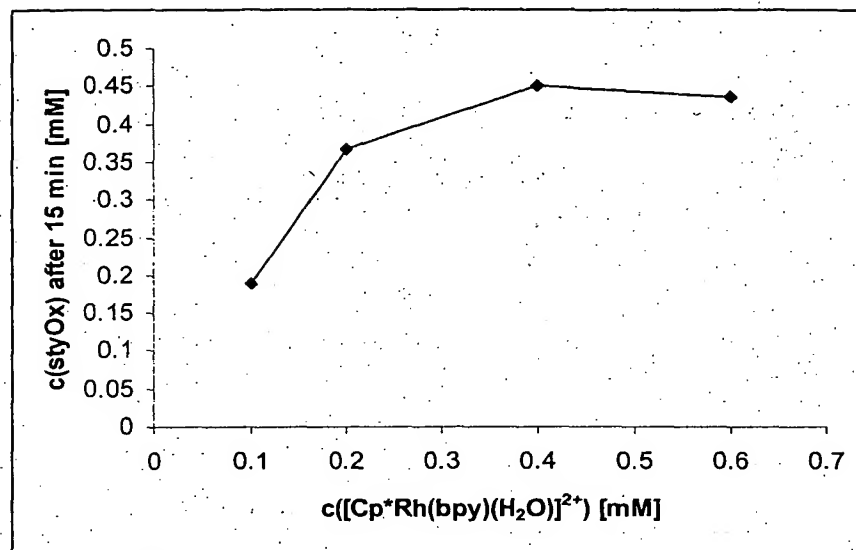


Figure 13: Styrene oxide concentration after 15 min incubation on variation of c([Cp*Rh(bpy)(H₂O)]²⁺).

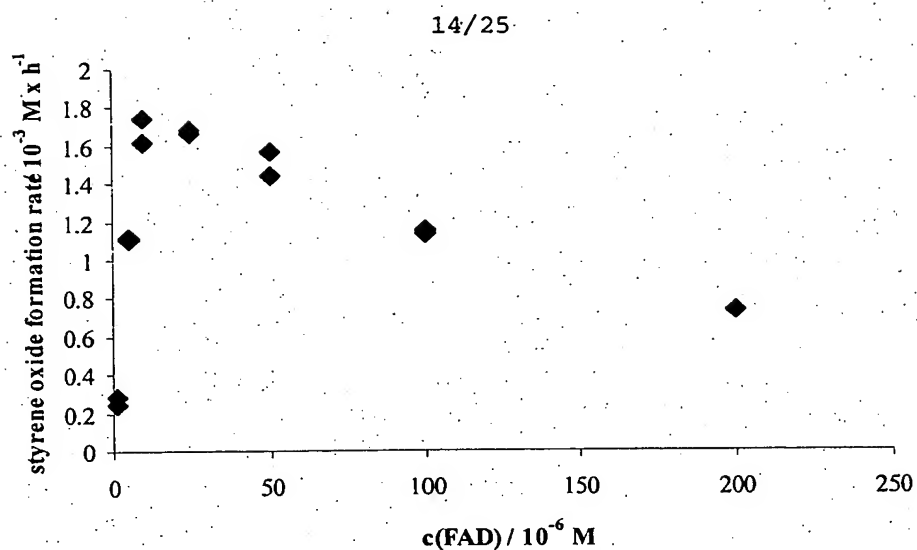


Figure 14: Styrene oxide formation rate as a function of $c(\text{FAD})$.
 $c([\text{Cp}^*\text{Rh}(\text{bpy})(\text{H}_2\text{O})]^{2+}) = 0.2 \text{ mM}$; $c(\text{StyA}) = 1.25 \mu\text{M}$; Catalase 280 U;
 $c(\text{styrene}) = 2 \text{ mM}$; $T = 37^\circ\text{C}$.

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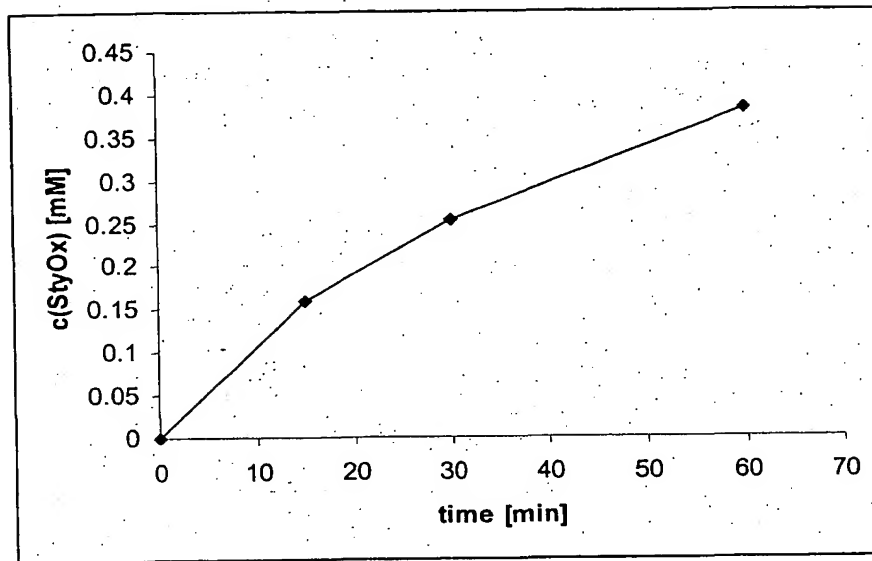


Figure 15: Styrene oxide (StyOx) formation using immobilized StyA.

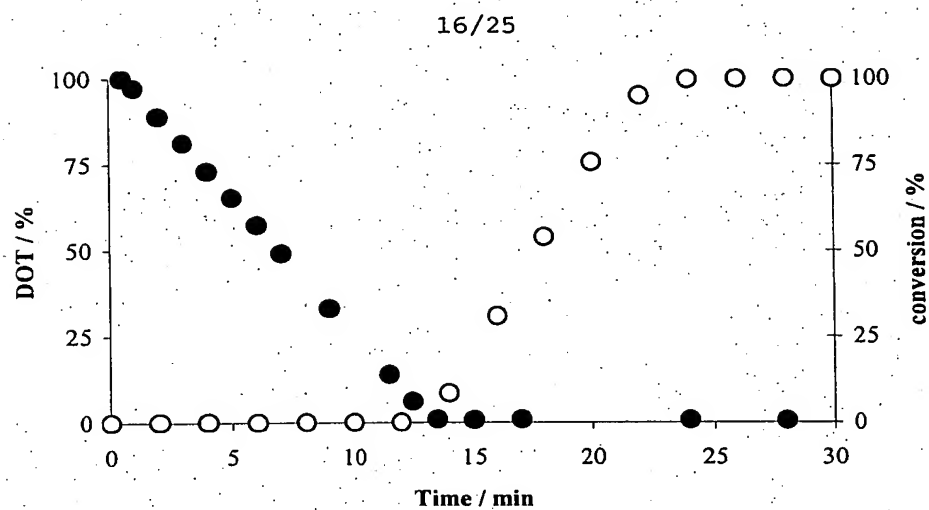


Figure 16: Time course of dissolved oxygen (DOT) (●) and c(FADH₂) (○) while incubating with [Cp*Rh(bpy)(H₂O)]²⁺ (0.2 mM) in sodium formate (0.15 M) at 37°C.

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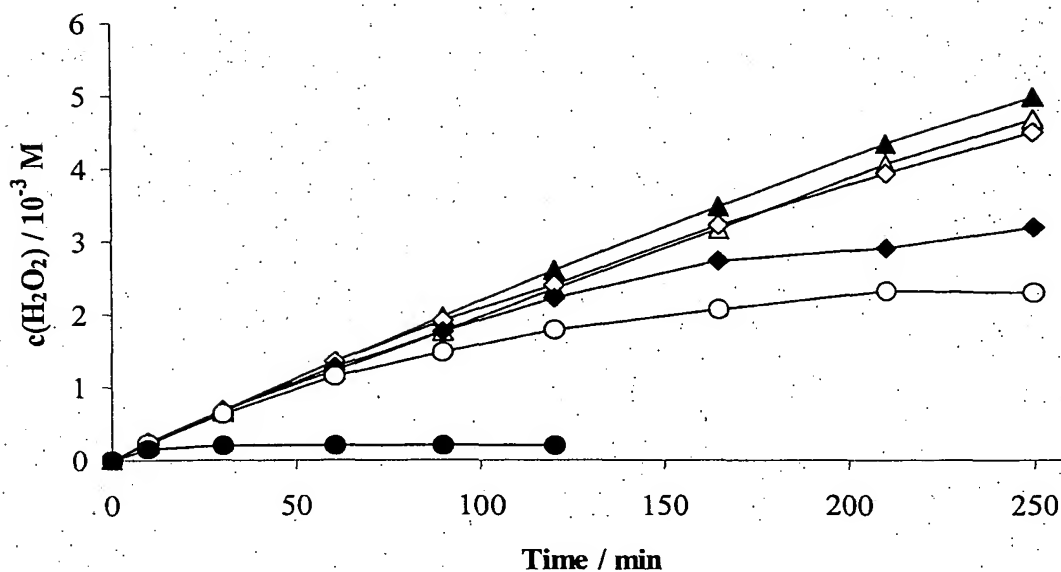


Figure 17: Time course of hydrogen peroxide formation at different ratios $[\text{Cp}^*\text{Rh}(\text{bpy})(\text{H}_2\text{O})]^{2+} / \text{FAD}$. $c([\text{Cp}^*\text{Rh}(\text{bpy})(\text{H}_2\text{O})]^{2+}) = 19 \mu\text{M}$, $c(\text{NaHCO}_2) = 0.15 \text{ M}$, $T = 37^\circ\text{C}$, $c(\text{FAD}) = 0 \mu\text{M}$ (●), $10 \mu\text{M}$ (○), $20 \mu\text{M}$ (◆), $50 \mu\text{M}$ (◇), $100 \mu\text{M}$ (▲), $200 \mu\text{M}$ (△).

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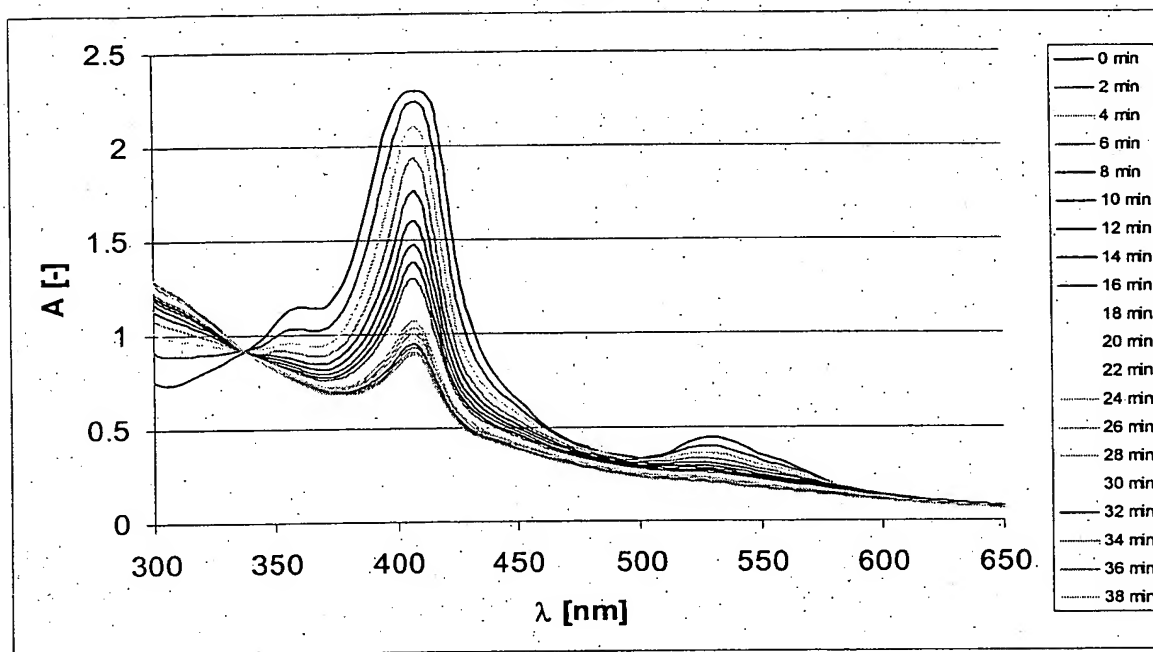


Figure 18: UV-spectra of a 50 μM Cyt C solution in the presence of 1 mM H₂O₂.

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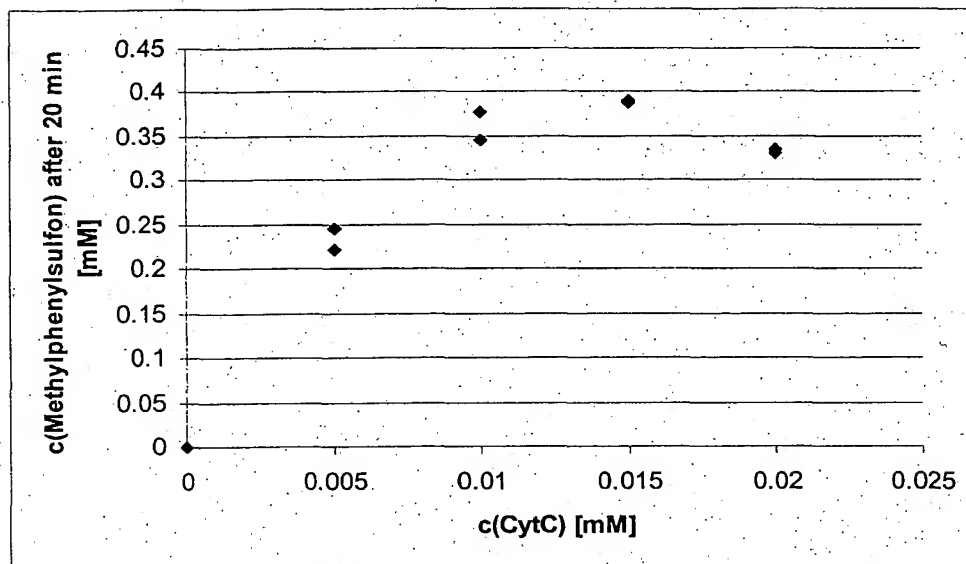


Figure 19: Dependence of the CytC-catalyzed sulfoxidation efficiency on c(CytC).

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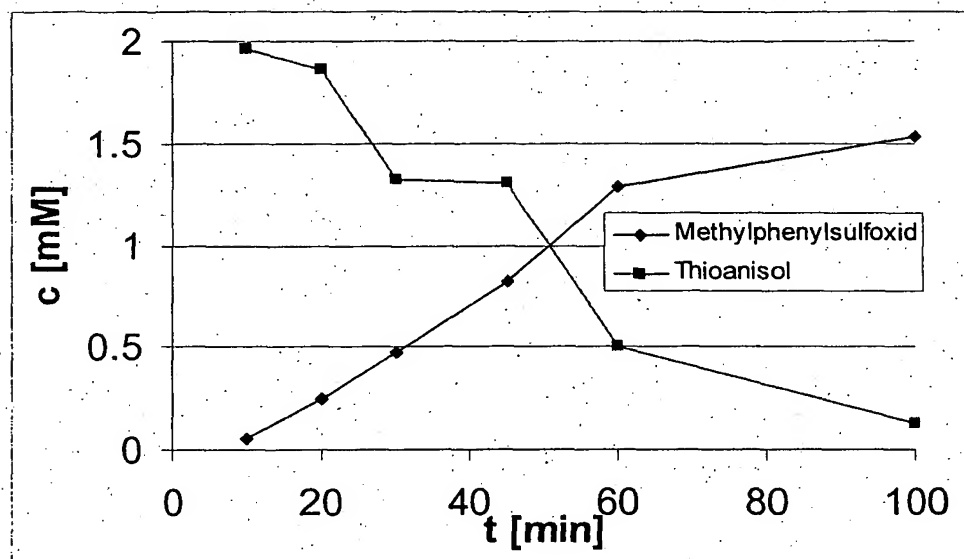


Figure 20: Time-course of CytC-catalyzed sulfoxidation of thioanisol with *in situ* generation of hydrogen peroxide by $[\text{Cp}^*\text{Rh}(\text{bpy})(\text{H}_2\text{O})]^{2+}$.

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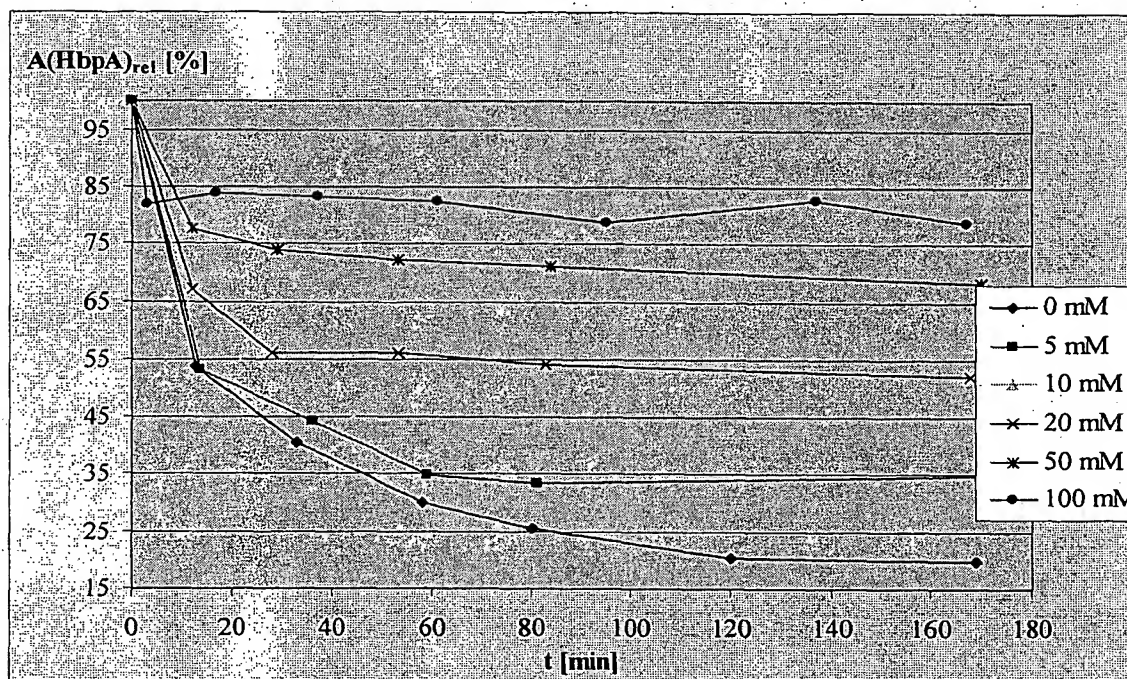


Figure 21: Residual HbpA activity while incubation with $[\text{Cp}^*\text{Rh}(\text{bpy})(\text{H}_2\text{O})]^{2+}$ and varying NH_3 concentrations.

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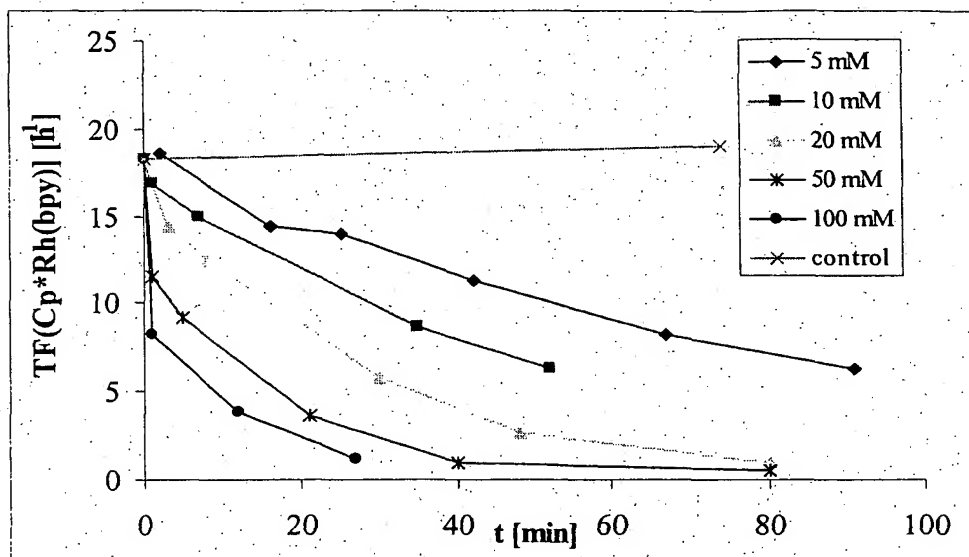


Figure 22: Inhibition of formate driven NADH regeneration catalyzed by $[\text{Cp}^*\text{Rh}(\text{bpy})(\text{H}_2\text{O})]^{2+}$ under varying NH_4^+ concentrations.

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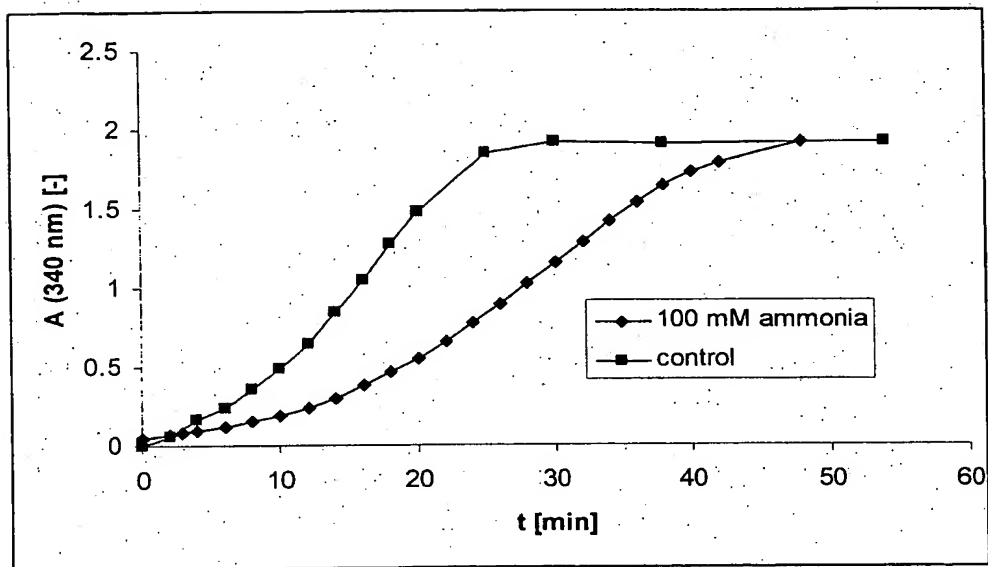


Figure 23: Feasibility of electrochemical NADH regeneration in NH_4^+ containing buffers.

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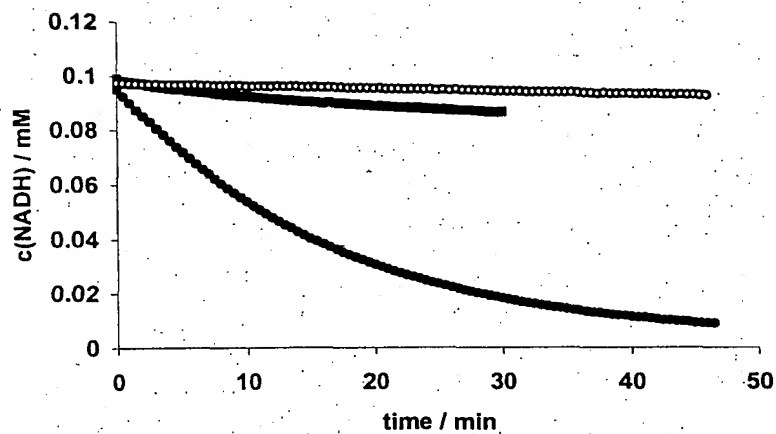


Figure 24: Oxidation of NADH by $[\text{Cp}^*\text{Rh}(\text{bpy})(\text{H}_2\text{O})]^{2+}/\text{FAD}$: $c(\text{NADH})_0 = 0.1 \text{ mM}$; $T = 30^\circ\text{C}$; (■) only $[\text{Cp}^*\text{Rh}(\text{bpy})(\text{H}_2\text{O})]^{2+}$ (0.01 mM); (○) only FAD (0.04 mM); (●) both $[\text{Cp}^*\text{Rh}(\text{bpy})(\text{H}_2\text{O})]^{2+}$ (0.01 mM) and FAD (0.04 mM).

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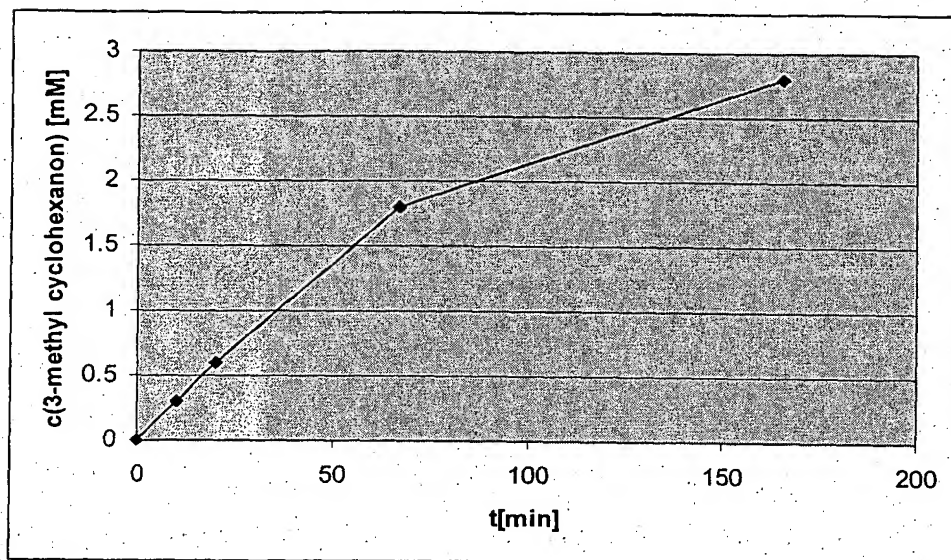


Figure 25: Time course of the oxidation of 3-methyl cyclohexanol catalyzed by alcohol dehydrogenase from *Thermus sp.*. The necessary oxidized nicotinamide coenzyme was in situ generated from NADH.